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POLARIZATION AND THE SIGN OF THE LONG-WAVELENGTH COTTON-EFFECTS IN CHROMOPHORES OF SYMMETRY C_2

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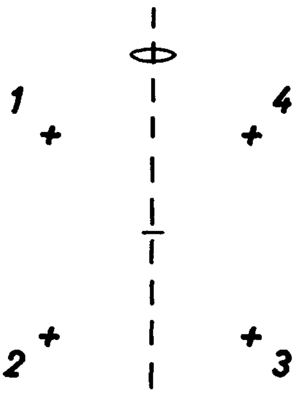
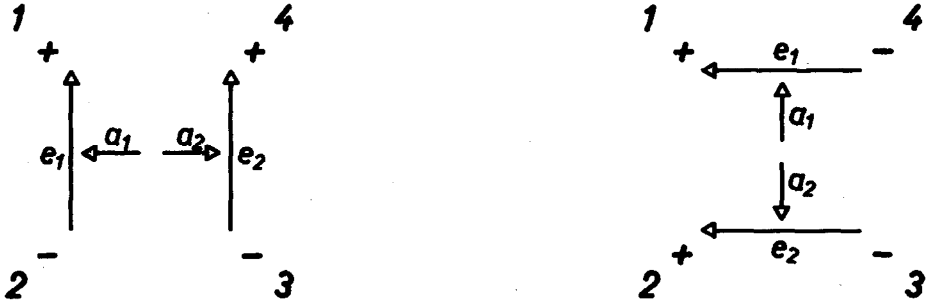
It appears that in the long-wavelength CD (or ORD) spectrum of a wider variety of chiral molecules of effective symmetry C_2 the sign of a given Cotton-effect depends solely on the chirality of the chromophore and on the polarization of the transition with respect to the twofold axis of symmetry. In transitions of symmetry A the electric dipole and magnetic dipole transition moments lie parallel or antiparallel to the twofold axis. Transitions of symmetry B are polarized perpendicularly. If the chirality is right-handed transitions of symmetry A lead to negative Cotton-effects, transitions of symmetry B to positive ones.

These conclusions are supported by a large number of SCF-LCAO-MO calculations with and without configuration interaction: a) On helicenes, within the PPP-approximation1,2); b) On diones3) and dienes4) within the CNDO approximation. Similar results are also obtained by simpler means5), although a many-electron treatment including configuration interaction enhances the effect. Wherever absolute steric configurations are known one finds an agreement with experiment6). It seems that the enone chromophore also follows the rule, displaying pseudo-C_2 symmetry7).

It is obvious that the nodal properties of the wavefunctions play a decisive role in bringing about these results. It may perhaps be visualized qualitatively by a very crude model (see figure). Numbers 1,2,3,4 denote schematically the position of atoms, for instance in a cis-diene, or of groups of atoms, for instance in a helicene. In the ground state the sign of the wavefunction be everywhere positive. In the simplest possible excited state of symmetry A a node bisects the twofold



ground state



excited state A

excited state B

Figure

axis. In the excited state of symmetry B the twofold axis lies within a node. We consider the electric dipole transition moment to be built up solely from "nearest-neighbor" increments, as shown by vectors $\vec{e}_1$ and $\vec{e}_2$. Similarly we neglect the local contributions of groups 1,2,3,4 to the magnetic transition moment, and we choose the origin of the angular momentum operator to lie on the symmetry axis as shown by the position vectors $\vec{a}_1$ and $\vec{a}_2$. At first we imagine the molecule to lie in the plane of the drawing. We then lower 1 below the plane and lift 4 above the plane, keeping 2 and 3 in the plane. Thereby the molecule acquires right-handed chirality. For the A-transition the vector $\vec{e}_1$ now points below the plane, $\vec{e}_2$ above the plane. We then obtain for the electric and magnetic transition moments respectively

$$\vec{r} = \vec{e}_1 + \vec{e}_2$$

$$\vec{m} = (\vec{a}_1 \times \vec{e}_1) + (\vec{a}_2 \times \vec{e}_2)$$

and for the rotational strength

$$R_A = \vec{e}_1 \cdot (\vec{a}_2 \times \vec{e}_2) + \vec{e}_2 \cdot (\vec{a}_1 \times \vec{e}_1).$$

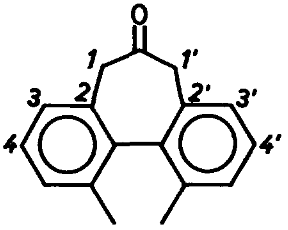
R_A may be shown by elementary vector geometry to be negative. If, on the other hand, 1 goes up and 4 goes down, leading to a left-handed chirality, R_A becomes positive.

For the B-transition $\vec{e}_1$ points downwards, whereas $\vec{e}_2$ still lies in the plane. We find, as above

$$R_B = \vec{e}_1 \cdot (\vec{a}_2 \times \vec{e}_2) + \vec{e}_2 \cdot (\vec{a}_1 \times \vec{e}_1).$$

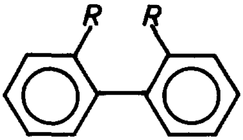
Both terms are positive, so that R_B is positive. A change from right-handed to left-handed chirality again implies a change in the sign of R_B. This model is admittedly very limited and crude, but it may give an indication of the reasons for the observed regularities.

As an example for the possibly quite general applicability of the C_2-rule here described we consider the case of the dimethylbiphenyl bridged ketone[8]



Neither the sector rules for ketones, nor the exciton model make any predictions concerning the absolute sign of the longest-wavelength Cotton-effect, attributed to a transition of the n-π*-type. We assume right-handed chirality, that is, atoms 1,2,3 to be lowered, atoms 1',2',3' to be lifted above the plane described by the carbonyl group and atoms 4 and 4'. Quite obviously the n-π*-transition is of symmetry A and should therefore display a negative Cotton-effect. This is found to agree with experiment.

On the other hand, we suspect that the rule should be applied very cautiously to biphenyls of the type



If the substituents R are weak, the chromophore may, to a large extent, behave as if it effectively had D_2 symmetry. The stronger the substituents, the more markedly should C_2 symmetry govern the electronic properties.

The spectroscopic utility of the rule stated here resides in the possibility of determining the polarization of transitions from the sign of the Cotton-effect, if the absolute configuration is known. However, it is conceivable that the rule is not valid for all higher-lying transitions. Our studies have mainly been concerned with transitions which, in the corresponding hypothetical planar molecule, would be labeled n-π^* or π-π^*. For stereochemical investigations this possible limitation should have secondary importance.

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